

California Environmental Protection Agency
 **Air Resources Board**

**PROCEDURE FOR
THE DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN
PARTICULATE MATTER USING GAS CHROMATOGRAPHY/MASS
SPECTROMETRY**

**Standard Operating Procedure No. MLD 144
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Standard Operation Procedure for the Determination of Polynuclear Aromatic Hydrocarbons in Particulate Matter using Gas Chromatography/Mass Spectrometry

1. Scope

- 1.1 This Standard Operation Procedure (SOP) describes the identification and quantification of polynuclear aromatic hydrocarbons (PAHs) extracted from vehicle exhaust particulate matter (PM) collected on filters and analyzed using gas chromatography /mass spectrometry (GC/MS).
- 1.2 The target analytes in this GC/MS method are listed in Table 1.
- 1.3 The individual PAH detection limit for the filter extract is equal to or less than 0.1 ng/mL depending on the extent of interference and the sensitivity of each PAH's. The detection limit for the mass of each PAH on the filter can range from 0.03 ng to 5 ng depending upon the solvent purity, background interferences, and analytical conditions (variation of final extraction volume and GC injection volume).

2. Summary of Test Method

- 2.1 PAHs from particulate matter are collected on different types of filters including Teflon coated glass fiber filter and quartz fiber filter.
- 2.2 PAHs on the filters are solvent extracted and analyzed by gas chromatography/mass spectrometry (GC/MS).
- 2.3 Prior to extraction, known amounts of recovery standards (RS) are added to the filter sample. The filter sample is then extracted either with an accelerated solvent extraction (ASE) or a Soxhlet extractor using dichloromethane as the solvent.
- 2.4 PAHs are identified by their GC retention times and characteristic mass peaks. These recovery standards and target analytes are quantified using an internal standard method.

- 2.5 The PAH mass (ng) on the filter is calculated by multiplying the extract volume and its concentration, and is corrected for its recovery efficiency.
- 2.6 A flow chart of this method is shown in Figure 1.

3. Terminology (Definitions)

- 3.1 Amu (Atomic mass unit) - Unit of mass to express atomic or molecular masses.
- 3.2 Internal Standard (IS) – Internal Standard is usually a deuterated compound added to a sample extract in a known amount and is used to calibrate concentrations of other sample analytes. The internal standard must not be the target analytes.
- 3.3 Method Detection Limit (MDL) – the minimum concentration of a substance that can be measured and reported with confidence and the value is above zero.
- 3.4 Polynuclear Aromatic Hydrocarbons (PAHs) – aromatic hydrocarbons with two or more fused aromatic rings.
- 3.5 Recovery Standard (RS) – Recovery Standard is usually a deuterated compound added to a sample in known amount prior to solvent extraction. The measured amount of the recovery standard after extraction is compared to its theoretical (calculated) value to establish the extraction efficiency and a correction factor for a specified analyte.

4. Limitations and Interferences

- 4.1 The target analytes are not limited to those listed in Table 1, but can increase or decrease, depending on the availability of National Institute of Standards and Technology (NIST) reference materials or traceable standards.
- 4.2 The GC/MS analysis is not limited to PAHs collected on filter media. With proper extraction and sample preparation, the GC/MS method can identify and quantify PAHs from other sample collection media and emission sources.
- 4.3 Quantification of the target analyte is subject to interference from compounds that have the same m/z with the same retention time region in the analysis.

- 4.4 Closely eluting compounds with the same quantification ions may not have enough peak resolution for quantification.
- 4.5 Teflon filters can only be extracted by Soxhlet extraction. The Accelerated Solvent Extraction (ASE) dissolves the support ring and causes contamination.

5. Safety

- 5.1 Many chemicals, especially PAHs, are toxic and/or carcinogenic. These chemicals must be handled extremely carefully with proper protection in the fume hood.
- 5.2 Solvents such as acetone and hexane are flammable and harmful. Handle these solvents in the fume hood.
- 5.3 Dichloromethane (DCM) is a potential carcinogen and can penetrate gloves. Handle DCM in the fume hood and avoid direct contact with skin.
- 5.4 The ASE is under high pressure (~ 1,600 psi) during operation and must remain inside the fume hood.

6. Equipments and Apparatus

- 6.1 Accelerated Solvent Extractor (or pressurized fluid extractor)

The PM filter extraction is performed with the Dionex Accelerated Solvent Extractor (ASE) Model 300. The extractor is capable of using different sizes of extraction cells and allows automatic mixing and delivery of up to four separate solvents.

- 6.2 Soxhlet Extraction

The Soxhlet extraction apparatus is shown in Figure 2. The extractor must include the following components:

- 6.2.1 A chiller to control the coolant temperature to as low as 5 °C.
- 6.2.2 A heating mantle with a Variac to control solvent distillation rate.
- 6.2.3 A magnetic stirring bar or boiling chips to prevent solvent from superheating.

6.3 GC/MS Analytical System

The GC/MS analytical system includes a Thermo Electron Gas chromatograph (GC) model TraceGC and a Mass Spectrometer (MS) model TraceMS. The system includes the following components:

6.3.1 Autosampler

The autosampler, Thermo Electron autosampler model AS 2000, is capable of delivering consistent volumes for the sample and the internal standard. The autosampler can add IS to the sample prior to sample injection to the GC .

6.3.2 Gas Chromatograph (GC)

6.3.2.1 The GC oven is temperature programmable.

6.3.2.2 The sample inlet includes a large volume injector capable of injecting sample volume in the range of 1 μ L to 100 μ L, at a controlled rate (for example, 2 μ L/sec). The injector must be temperature-programmable and must be equipped with a solvent valve for venting volatile solvents.

6.3.2.3 The column is a 30 meter long x 0.25mm ID fused silica capillary column coated with a cross-linked phenyl methyl silicone. Any column with a similar separation capability can also be used.

6.3.3 Mass Spectrometry (MS)

The TraceMS is capable of producing electron impact spectra at +70 eV (nominal) and scanning the range of the specified quantification masses or m/z. A scan range of 40 to 500 m/z is adequate for PAH analysis.

6.3.3.1 Data Acquisition

The data acquisition is controlled by Xcalibur (Thermo Electron software), which searches any GC/MS runs for specific ions or reconstructed ions, and plots the intensity of the ions with respect to retention time or scan number.

7. Reagents and Materials

7.1 Gases

- 7.1.1 Helium, a carrier gas for GC/MS, at least 99.9995 % purity.
- 7.1.2 Nitrogen, at least 99.999% purity and free of PAHs contamination.
- 7.1.3 Compressed Zero Air, for ASE valve switching. It can be substituted by nitrogen gas.

7.2 Reagents

- 7.2.1 Dichloromethane (DCM), at least 99.8% purity. The PAHs levels in this DCM must be less than the method detection limits and suitable for PAH trace analysis at or below the part-per-billion.
- 7.2.2 Acetone, at least 99.9% purity.
- 7.2.3 Hexane, at least 99% purity.
- 7.2.4 NIST Reference Materials. Any NIST reference materials containing the target analytes can be used for calibration, for example, SRM 1491.
- 7.2.5 Deionized water, at least 5Ωm resistance.
- 7.2.6 PAH solution, 2000 µg/mL in DCM, Absolute Standards, Inc. Solutions from other sources are also acceptable as long as they contain PAHs of interest.
- 7.2.7 Deuterated PAHs

Deuterated PAHs are used as recovery and internal standards. The purity of these compounds shall be the highest whenever it is possible. The purities of these deuterated PAHs purchased from CDN are sufficient for the purposes.

7.3 Filters

Quartz fiber filter, glass fiber filter, and/or Teflon coated glass fiber filter such as Pallflex 7213 T60A20 are used for PM sampling.

- 7.4 Silica gel, 1 gram pre-cleaned silica gel packed in a 6 mL glass tube.

8. Preparation of Sample

- 8.1 Filters for PAH analysis are pre-cleaned with DCM via Soxhlet extraction prior to sample collection.
- 8.2 Load the filters in the cleaned Soxhlet extraction tube and clean the filters according to the procedure in section 9.3.
- 8.3 Remove the extraction tube. Purge the filters at room temperature with nitrogen gas till dry.
- 8.4 Any alternative cleaning procedure is acceptable as long as the background concentrations of the analytes are below the method detection limits.

9. Preparation of Apparatus

9.1 ASE Extractor Cell Cleaning

- 9.1.1 Inspect the integrity of the extraction cell, such as the Teflon O-ring. Replace the seals when necessary.
- 9.1.2 If necessary, clean the cells. Rinse the cell parts with DI water and acetone. Air dry the cell parts or oven dry at 100°C. Cell disposable filters can be cleaned with DCM via Soxhlet extraction. If the disposable filter needs to be replaced, conduct extraction once (dummy extraction) to ensure there is no PAH contamination in the disposable filters.
- 9.1.3 Sonicate the borosilicate glassballs (cell fillings) with DI water in a clean beaker for at least 30 minutes. Discard and drain the water. Repeat the procedure for the second time. Rinse the borosilicate glassballs with DI water, followed by acetone, hexane, and dichloromethane. Air dry or oven dry at 100°C in a PAH contamination free environment.

9.2 Glassware cleaning

All glassware can be cleaned by the following procedures:

- 9.2.1 Wash with detergent (Extran AP12. residue free or equivalent) and rinse with DI water during washing cycles in a washing machine.
- 9.2.2 Rinse the washed glassware three times with acetone, hexane and dichloromethane, in that order.

- 9.2.3 Dry the cleaned glassware in an oven at approximately 100 °C.
- 9.2.4 Alternative cleaning procedures can be used if the background concentrations for PAHs are below the method detection limits.
- 9.3 Soxhlet extractor cleaning
 - 9.3.1 Clean Soxhlet extractor, following sections 9.2.1 to 9.2.3.
 - 9.3.2 Assemble the cleaned Soxhlet extraction apparatus, as shown in Figure 2, with a thimble (if needed) in the extraction tube.
 - 9.3.3 Set the temperature of the chiller at approximately 6 °C for condensing DCM.
 - 9.3.4 Adjust the Variac to control the DCM distillation rate at approximately 3 cycles per hour. Continue distilling for at least 6 hours.
 - 9.3.5 Discard the solvent and dry the apparatus in the oven if desired.

10. Preparation of Standards for PAH Analysis

10.1 Preparation of Recovery Standards (RS)

The recovery standards (RS) consist of several deuterated PAHs for assessing the extraction efficiency. Each PAH is assigned with one of the RS. Each PAH species and its corresponding RS are listed in Table 2. Depending upon the availability of the deuterated compounds, the PAH's RS can be reassigned.

- 10.1.1 Accurately weigh each RS (approximately 0.01g).
- 10.1.2 Add all the weighed compounds to a 100 mL volumetric flask.
- 10.1.3 Dissolve the RS with DCM (< 100 mL) in the flask.
- 10.1.4 Add DCM to the 100mL mark to make a 100 µg/mL stock solution.
- 10.1.5 Pipet 1 mL of the 100 µg/mL stock solution, and dilute with DCM to the 100 mL mark. The dilution results in a 1 µg/mL solution and can be used for spiking the filter samples before extraction.
- 10.1.6 Continue diluting from the 1µg/mL solution with DCM to make deuterated PAH calibration standards for the GC/MS. Typical

concentrations for these standards are 0.1, 0.5, 1.0, 2.0, and 3.0 ng/mL.

- 10.1.6.1 To prepare a calibration standard for deuterated PAHs , pipet 10 mL 1µg/mL solution and dilute to 100 mL to make a 100 ng/mL solution.
- 10.1.6.2 Continue pipetting 0.5, 1, 2, and 3 to four individual 100 mL flasks to prepare 0.5, 1.0, 2.0, and 3.0 ng/mL solutions. Use the 1.0 ng/mL solution to perform 1:10 dilution to make a 0.1 ng/mL solution.
- 10.1.7 Use the 100 ng/mL recovery standard to make a solution to spike the filter samples if the sample extract needs to be concentrated more than four times. To calculate the volume of a recovery standard solution for spiking the filters, determine the desired concentrations of recovery standards in the extract including the final extract volume. The final concentrations should be within the calibration range of the calibration standards.
- 10.1.8 The integrity of the recovery standard requires frequent checking. The concentration of the recovery standard may change due to solvent evaporation, degradation, and any other reasons that can shorten its life.
- 10.1.9 Prior to extraction, check the concentration agreement between the deuterated PAH calibration standards and spiking solution by analyzing a freshly prepared QC solution of ~ 1 ng/mL from a spiking solution. If the results fall within 20 % of the expected values of each recovery standard, extract PM filters by following the procedures in section 11.
- 10.1.10 Correct the problems by preparing a new spiking solution and calibration standards from stock solution prior to extraction if the results exceed the 20% limit.

10.2 Preparation of PAH Calibration Standards

The calibration standards are obtained following a series dilution of the NIST Reference Material, for example, SRM 1491, consists of 23 certified PAHs and one non-certified PAH. The compounds along with their concentrations for each level of calibration standards are listed in Table 3. Other calibration standards including gravimetrically prepared standards from pure compounds are acceptable.

- 10.2.1 The PAH calibration concentrations diluted from SRM 1491 range

from 0.05 ng/mL to 3.0 ng/mL. The actual PAHs' concentrations may vary, depending on the SRMs being used. Table 3 lists the diluted concentration from SRM 1491.

- 10.2.2 Use a syringe to take out 250 μ L of SRM 1491 solution. Insert the solution to a 100 mL flask and dilute with DCM to prepare a stock solution.
- 10.2.3 Pipet 1, 2, 3, 5, 10, and 15 mL of stock solution to 5 individual 100 mL flask and dilute with DCM to the mark. The procedure will yield six calibration standards and the concentrations of these standards are listed in Table 3. The procedure may vary due to availability of SRMs.

10.3 Preparation of deuterated PAH Internal standards (IS)

Five deuterated PAHs are selected as IS for the determination of PAH concentrations. Each analyte has one, in some cases two, of the IS assigned for quantification. The area of the analyte's quantification ion is a ratio to that of the IS to determine the concentration of the analyte. The corresponding IS for each analyte is listed in Table 4.

- 10.3.1 The ISs used in this method are: acenaphthene-d10, phenanthrene-d10, pyrene-d10, chrysene-d12, and perylene-d12.
- 10.3.2 Should interference be found in the quantification ions of any IS (such as chrysene-d12 and pyrene-d10), use another deuterated PAH as IS.
- 10.3.3 The following procedure is a typical way of preparing the IS solution. Weigh the four ISs individually (approximately 0.05 g) and add all weighed ISs into a 100 mL flask.
- 10.3.4 Dissolve the ISs with DCM. When the solid compound is dissolved completely, add more DCM to the 100 mL mark to prepare a ~ 500 μ g/mL stock solution.
- 10.3.5 Pipet 1 mL of the stock solution into a 100 mL flask and dilute with DCM to make a 5 μ g/mL solution. Pipet 2 mL of the 5 μ g/mL into a 100 mL flask and dilute with DCM to make a 100 ng/mL solution.
- 10.3.6 Pipet 5 mL of the 100 ng/ mL solution into a 100 mL flask and dilute with DCM to the mark to prepare an IS solution at a concentration of 5 ng/mL for each compound.

10.4 Preparation of QC standards

QC standards can be volumetrically diluted from a commercially available or a NIST SRM PAH standard. The PAH component's QC concentration shall be in the mid range of the prepared GC/MS calibration standards. The suggested QC standard concentration is approximately 1.0 ng/mL.

- 10.4.1 To prepare the QC solution for the PAH analysis, a series of dilutions are needed. The actual dilution procedure is dependent upon the concentration of the solution. The following procedure is an example for diluting a 2 mg/mL PAH solution.
- 10.4.2 Use a syringe and take a 250 μ L aliquot of the 2 mg/mL PAH standard into a 100 mL flask. Dilute the solution to the mark with DCM to make a 5.0 μ g/mL solution.
- 10.4.3 Pipet 1mL of the 5 μ g/mL solution and dilute to the 100 mL mark with DCM to prepare a 50ng/mL solution.
- 10.4.4 Continue pipetting 2 mL of the 50 ng/mL solution and dilute to the 100 mL mark with DCM to prepare a 1.0 ng/mL QC solution.

11. Procedures for PAH Quantification

11.1 Sample Extraction

The following section describes the procedures to operate the Dionex ASE300 and extract PAHs collected on PM filter samples. The procedures should be modified if different sample collection media are used.

- 11.1.1 Visually examine the integrity of the cell parts, including Teflon O-ring, frits, and disposable filters. These parts provide seals needed for the pressurized and heated extraction cells.
- 11.1.2 Place the sample filter in the cell with tools (for example, forceps). Avoid direct contact between the forceps and the sample collection side of the filter to reduce potential losses of the analytes and to avoid cross contamination among samples. Should direct contact occur, rinse the forceps with acetone followed by hexane and DCM prior to next use, or use a clean forceps.
- 11.1.3 Spike the sample filter with the RS. The RS volume and concentration varies, depending upon the "estimated" amount of the PAHs collected on the filters. If such an estimate can not be

made, assume the extract will not be concentrated. For example, spike 25 μ L of a 1 μ g/ mL RS solution resulting in RS concentration of 0.5 ng/ mL in the 50 mL extract. Spike 50 μ L of 100 ng/mL RS solution resulting in RS concentration of 1.0 ng/mL in the 5 mL final extract solution if the volume of ASE extract, typically ~ 50 mL, is reduced 10 times.

- 11.1.4 Pack the cells with borosilicate glass balls. Do not over-pack the cells. Provide good seals for the cells to reduce potential extraction failure. Keep the threads and sealing surface clean.
- 11.1.5 Open the cylinder gas valves. Load the extract bottles. Use the ASE extraction software to set up the extraction schedule and method. Start the extraction.
- 11.1.6 PAHs can be photosensitive and volatile. After extraction, measure the sample extract volume. Transfer the sample extracts to an amber bottle and store the bottle of extract in a refrigerator until analysis.

11.2 Solvent Reduction and Clean-up

Solvent reduction is used to concentrate the extract after the solvent extraction and to increase the method sensitivity. If the concentration is needed, estimate Recovery Standard's (RS) final concentration prior to spiking. The expected RS final concentration shall be in the linear range of the calibration standards. Perform dilution if the analytical results are outside the calibration range.

11.2.1 Nitrogen blow-down

The filter extract is concentrated by flowing nitrogen gas on top of the extract solution. This will evaporate the excess DCM and thus reduce the volume of the extract.

- 11.2.2 Connect the mini-vap to the nitrogen gas source and allow nitrogen to flow through. The nitrogen can be either from a liquid nitrogen boiloff or from a zero nitrogen cylinder as long as the nitrogen gas is free of PAH contamination.

- 11.2.3 The following procedure is an example for concentrating an extract 4 times.

- 11.2.3.1 Pipet 4 mL of the filter extract to a conical interior bottom vial with graduations. Start the nitrogen flow slowly to avoid splashing the solution.

- 11.2.3.2 Stop nitrogen flow when the solution is below the 1.0 mL mark. Never allow the solution to dry out.
- 11.2.3.3 DCM to wash down any deposit and increase the total volume to the 1.0 mL mark.
- 11.2.3.4 Other concentration ratios are acceptable as long as the PAH interference in the DCM is below the filter extract's detection limits. If DCM interference becomes a problem, blank subtraction may be necessary. Carefully analyze 3 blank solutions to determine the PAH concentrations.
- 11.2.3.5 The concentrated filter extract is ready for GC/MS analysis.

11.2.4 Clean-up

Perform a clean-up procedure if matrix interference becomes problems for PAH quantification. This method utilizes silica-gel to eliminate interferences. An example for the cleaning procedure is as follows:

- 12.2.4.1 Condition silica-gel (1 gram silica-gel packed in 6 mL glass tube) with 2 mL of DCM and followed by hexane filled to the top of the tube.
- 12.2.4.2 Add 250 uL sample extract to the silica-gel when hexane is almost completely eluting out of the top of the tube.
- 12.2.4.3 Immediately add 2 mL of hexane to the solution and when the solution is almost disappearing from the top, add 3 mL of DCM.
- 12.2.4.4 Collect the PAHs fraction when the DCM is eluting from the silica-gel tube.
- 12.2.4.5 Follow the procedure as described in section 12.2.1 to concentrate the DCM solution and the concentrated filter extract is ready for GC/MS analysis.

11.3 GC/MS Tuning

The following sections describe the procedures and conditions of conducting GC/MS analysis for PAHs.

11.3.1 Prior to the GC/MS analysis, the MS must pass its auto-tuning criteria with FC-43 to demonstrate that the instrument passes all tuning criteria. The criteria include ion abundance, mass resolution, and mass calibration.

11.3.2 Auto-tune also automatically adjusts ion source parameters for optimum performance.

11.4 GC Operating Conditions

11.4.1 Typical autosampler parameters include:

Internal standard volume: 5.0 µL
Sample volume: 30.0 µL
Injection speed: 3.0 µL/sec
Syringe size: 100 µL

11.4.2 Typical GC operating conditions include the following:

GC column: 30 meter long x 0.25mm ID, DB-5 fused silica capillary column
Oven method: initial temperature: 40 °C for 2 minutes
Temperature ramping rate: 10 °C/min
Final temperature: 300 °C and hold for 10 mins.
Carrier gas: helium with a constant flow rate at 1.20 mL/min.

11.4.3 Sample introduction is operated on a Programmable temperature and volume (PTV) large volume injection mode. A typical sample inlet method includes an initial condition and four phases. The Injection phase allows the sample to be introduced into the inlet at a low temperature with a vent valve open to reduce the excess DCM vapor volume and concentrates the non-volatile analytes inside the injector. Evaporation phase allows further reduction of the solvent volume. Transfer phase transfers the sample to the GC column at a higher temperature. Finally, the inlet undergoes the Cleaning phase. The following is a typical sample injection method:

Initial conditions:

Base temperature: 35 °C
Split flow rate: 150 mL/min
Solvent valve temperature: 140 °C.
Constant purge: on

Injection phase:

Injection time: 0.3 min

Vent flow: 150 mL/min

Evaporation phase:

Evaporation temperature ramping rate: 10°C/sec

Evaporation temperature: 40 °C

Evaporation time: 0.2 min

Transfer phase:

Transfer temperature ramping rate: 14.5 °C/sec

Transfer temperature: 300 °C

Transfer time: 0.2 min

Cleaning Phase:

Clean rate: 14.5 °C/ min

Clean temperature: 325 °C

Clean time: 25.0 min

Clean flow: 30 mL/min

11.5 MS Operation Conditions

- 11.5.1 The mass spectrometer is operated on a positive electron impact (EI+) mode. The typical settings for the MS include:

Source temperature: 250 °C

GC interface temperature: 300 °C

Emission current 350 µA

Electron Energy: 70.0 V (nominal)

Detector voltage: 350.0 V

- 11.5.2 The MS can be operated under either Selective Ion Monitoring Mode (SIM) or Full Scan Mode. SIM is usually used for quantification and Full Scan can be used for both compound identification and quantification. The primary (or quantifier) and secondary (or qualifier) ions for quantifying each analyte and each internal standard in the SIM mode are listed in Tables 5 and 6, respectively. For the Full Scan, the mass scan range is 50 to 500 amu at a scan rate of one second per scan.

11.6 Calibration Curve Construction

- 11.6.1 Before the calibrating procedure, tune the mass spectrometer according to manufacturer's instructions, as described in Section 11.2.
- 11.6.2 Set GC/MS operation conditions in accordance with sections 11.3 and 11.4.

- 11.6.3 Sequentially analyze the calibration standards by SIM mode.
- 11.6.4 Construct the calibration curves according to Section 12.1. Check the r^2 of linear regression. If the r^2 is not greater than the specified value (0.99), recalibrate the GC/MS system or correct any problem.
- 11.6.5 The GC/MS system shall be recalibrated whenever results of the quality control (QC) standard fail to meet the tolerance levels specified in section 14.

11.7 PAH Analysis

- 11.7.1 Prior to PAH analysis, allow the calibration standards (or RS if assessing recovery efficiency), the extract samples, the IS, and the QC solutions to reach room temperature.
- 11.7.2 Clean and fill the GC pre-cleaning and post-cleaning vials for the autosampler with DCM. All sample vial septa for GC analysis must be Teflon to avoid PAH contamination.
- 11.7.3 Load the DCM blank, calibration standards, sample extracts, IS, and QC samples to the GC/MS autosampler. Start the analysis with the DCM blank followed by calibration standards to establish GC/MS background and performance
- 11.7.4 Analyze at least one QC and one duplicate sample for every 10 sample extracts.
- 11.7.5 Set up the sequence for sample analysis.

12. Quality Control (QC)

12.1 Calibration

- 12.1.1 GC/MS requires frequent calibration. Calibration is needed when starting an analysis or any QC failure, as described in section 12.4.
- 12.1.2 Check the correlation r^2 value for each PAH calibration curve. The r^2 value must be at least 0.99.

12.2 Failure to achieve the linearity requirement will require re-calibrating the GC/MS. If it fails after recalibration, the problems causing the failures should be corrected before any analysis can be reported.

12.3 Method detection limit for filter extract by GC/MS

Method detection limit (MDL) for a filter extract is defined as follows:

$$MDL(i) = t * SD (i)$$

where:

MDL(i) = method detection limit of PAH *i*

t = student's *t* value associated with a 98% confidence interval (section 12.3.1)

SD (i) = standard deviation of a replicate analysis of the lowest concentration standard for PAH component *i*

- 12.3.1 The Student's *t* value is dependent upon the degrees of freedom associated with the analysis. The degree of freedom of the analysis is equal to the number of replicate measurements, *n*, of the lowest concentration standard, minus one. An abbreviated table of values of *t* associated with a 98% confidence interval is shown below^(ref:4).

Degrees of Freedom (n-1)	t-value
4	3.7
5	3.4
6	3.1
7	3.0

- 12.3.2 For reporting, the method detection limit for the filter extract is set between 0.03 and 0.1 ng/mL. The reporting limit varies for each PAH's. The method detection limit for PAH mass on the filter can vary due to a variation of the final extract volume and analytical conditions. The filter extract detection limit should be verified annually or when the method is modified with potential influence on the detection limits.
- 12.3.3 The MDL for the PAH's must be below the reporting limit for each PAH's. If the calculated MDL of any PAH compound is above its reporting limit, the sources of the problems must be corrected and the MDL re-determined.
- 12.3.4 If the calculated MDL for filter extract is less than 0.03 ng/mL, SLB may set its reporting limit at the calculated MDL, or any level in between MDL and 0.03ng/mL. Any results below the MDL for the filter extract will be reported as "<L ".

- 12.3.5 For the purpose of calculating the total PAH mass, the concentrations of all compounds below the MDL are considered to be zero.

12.4 QC sample analysis

A QC sample is analyzed after calibration, after every 10 samples, and at the end of a sample set. If a QC failure occurs, the sources of the problems must be corrected before conducting any additional sample analysis.

- 12.4.1 Not all PAHs are monitored for quality control purposes. The choice of QC compounds depends upon the composition of commercially available standards and the retention times of the PAHs. This SOP uses the following PAHs to determine the performance of the GC/MS: naphthalene, acenaphthene, fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, and benzo[g,h,i]perylene. If the recovery standard is analyzed separately, three deuterated PAH: naphthalene-d8, anthracene-d10, and benzo[g,h,i]perylene-d12 are used for GC/MS performance check
- 12.4.2 Analyze the QC standards to determine the concentrations of these QC compounds.
- 12.4.3 The QC limit is 20% from the calculated concentration for each component in the QC standards. The QC is considered "pass" if the QC result is within 20% of the calculated concentration. Any result outside 20% is considered as a QC "failure". Problems causing a QC failure must be determined and corrected before further samples are analyzed.

12.5 Blank Analysis

A DCM sample must be analyzed at the beginning of the sequence of the analysis. The PAH level in the DCM must be below the PAH's MDL before proceeding to instrumental calibration or sample analysis.

12.6 Replicate Analysis

For each set of samples, perform a replicate sample analysis at least once or after every 10 sample analyses. The difference of the two replicate results for QC compounds listed in section 12.4.1 must be within 10% of their mean.

12.7 PAH identification

Identify the various PAHs in Table 1 from their retention times and mass spectra. Confirmation of a PAH can be obtained by matching the retention time and full scan MS of the GC/MS analysis with a calibration analysis. When comparing the criteria below must be met:

- 12.7.1 All characteristic ion peaks for the same PAH must have retention times within 0.01 min of one another.
- 12.7.2 The area ratio of the secondary to primary ion for the PAH must be within 5% when compared to the same ion area ratio from a calibration standard at approximately the same concentration. If such agreement cannot be made, choose secondary ions for calibration assuming the secondary ions are free of interferences or flag for "possible interference" in the final reports.
- 12.7.3 The GC retention time (from total ion chromatogram) must be within 0.03 min of that obtained for the same calibration standard.

13. Calculation

13.1 Calibration calculations:

- 13.1.1 After analysis of the standards, integrate the characteristic ion's (Table 5 and 6) peak area for each calibration compound and internal standard at the expected retention time. Figure 3 shows the chemical structure and the mass spectrum of each PAH compound in this analysis (Table 1). Figure 4 shows the total ion chromatogram (TIC) of a calibration standard.
- 13.1.2 Plot the response area ratio $R_{sp}(i)$ (y-axis) versus the amount ratio $Amt(i)$ (x-axis) to generate calibration curves for each PAH compound listed in Table 1:

Where:

$$R_{sp}(i) = A(i)/A(is)$$

$A(i)$ = area of compound i , and

$A(is)$ = area of internal standard.

and $Amt(i) = C(i)/C(is)$

$C(i)$ = concentration of compound i in the calibration standard,

$C(is)$ = concentration of the IS.

An example for a calibration curve is shown in Figure 5.

13.2 Linear least squares fit calculation

Obtain the linear least squares fit from the calibration curves. For each PAH i , the linear least squares fit can be expressed in the following form:

$$R_{sp}(i) = m(i) \times Amt(i) + b(i)$$

where

$m(i)$ = slope of linear equation for PAH i

$b(i)$ = intercept at the y-axis

13.3 PAH concentration calculation

From the equations in Sections 13.1.2 and 13.2, calculate the concentration of each PAH, $C(i)$, in ng/mL, in the filter extract using the area ratio ($R_{sp}(i)$) of the area for the sample of the PAH to that of the IS.

$$C(i) = [(A(i)/A(is) - b(i)) / m(i)] \times C(is)$$

13.4 Recovery efficiency calculation

The recovery efficiency can be calculated by comparing the original spiking deuterated PAH concentrations to the concentrations obtained from a GC/MS.

13.4.1 Follow the procedures described in sections 13.1-13.3 to determine the concentration of each deuterated PAH in the filter extract.

13.4.2 Calculate the original theoretical concentration of each deuterated PAH in the filter extract as follows:

$$Theo(i) = R_{Spike}(i) \times V(inj) / V(fext)$$

where

$Theo(i)$ = Calculated original theoretical concentration of deuterated PAH component i in the filter extract,

$R_{Spike}(i)$ = Concentration of deuterated PAH component i in spike solution,

$V(inj)$ = volume of spike solution injected on the filter prior to extraction, and

$V(fext)$ = final volume of filter extract

13.4.3 Calculate the recovery efficiency for each deuterated PAH as follows:

$$\% Recovery(i) = [C(i) / Theo(i)] \times 100\%$$

where

$\% Recovery(i)$ = recovery percentage of deuterated PAH component i

$C(i)$ = concentration of deuterated PAH component i obtained from the GC/MS, and

$Theo(i)$ = calculated original theoretical concentration of deuterated PAH component i in the filter extract.

- 13.4.4 If the calculated efficiency is less than 50% or higher than 150%, a remark or flag “recovery low” or “recovery high” must be noted on the analysis report.

13.5 Calculate the PAH mass in a filter sample

13.5.1 Calculate individual PAH mass

The individual PAH mass measured from each sample can be calculated by multiplying the extract volume and corrected for its extraction recovery efficiency.

- 13.5.2 The PAH mass can be calculated as follows:

$$PAH(i) = C(i) * V(fext) / \% Recovery(i)$$

where

$PAH(i)$ = measured mass (in ng) of PAH component i on filter,

$C(i)$ = concentration(in ng/mL, or ppb[w/v]) of PAH i obtained from GC/MS analysis,

$V(fext)$ = Final filter sample's extraction volume (in mL) prior to GC/MS analysis, and

$\% Recovery(i)$ = recovery percentage of PAH i .

- 13.5.3 For PAHs that have recovery efficiency greater than 100%, the recovery efficiency of 100% will be used to calculate the PAH mass.

14. Report

The report for each filter sample shall contain the identified PAH names and their individual measured masses, flags for high or low recovery efficiency, and flags for any possible interference for concentration determination. An example of the report is shown in Figure 6.

15. Reference Documents

1. California Environmental Protection Agency, Air Resources Board, Method 429: Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources.
2. US Environmental Protection Agency, Analytical Method for the Analysis of Semi-volatile Organic Compounds, Exhibit D
3. Desert Research Institute Compendium Method TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using gas Chromatography/mass Spectrometry (GC/MS).
4. Harris, Daniel C., "Quantitative Chemical Analysis", *W.H. Freeman & Co.*, 4th ed., 1995.

16. Revision History

Figure 1. Flowchart of Filter Sample Analysis

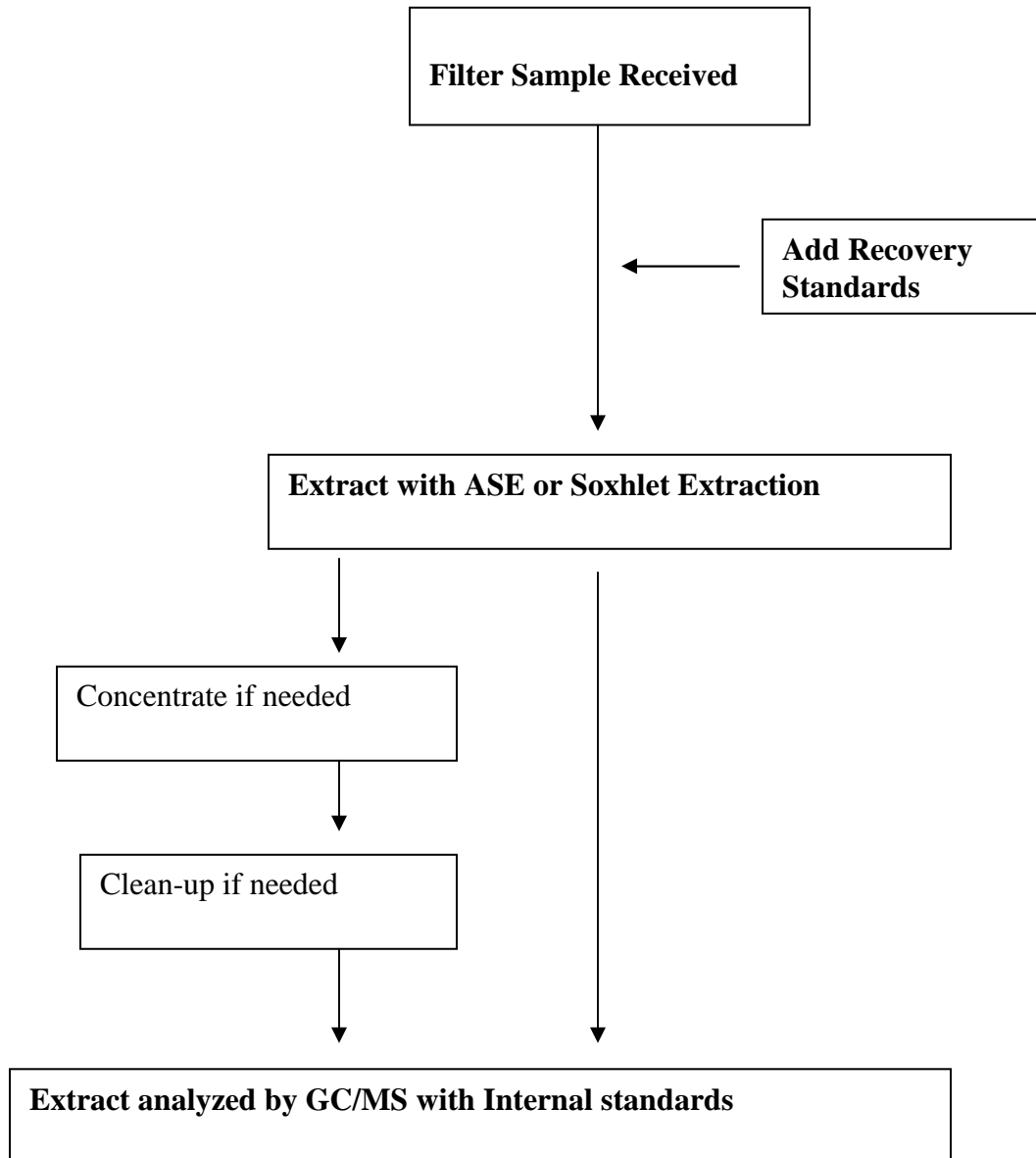


Figure 2. Soxhlet Extraction Apparatus

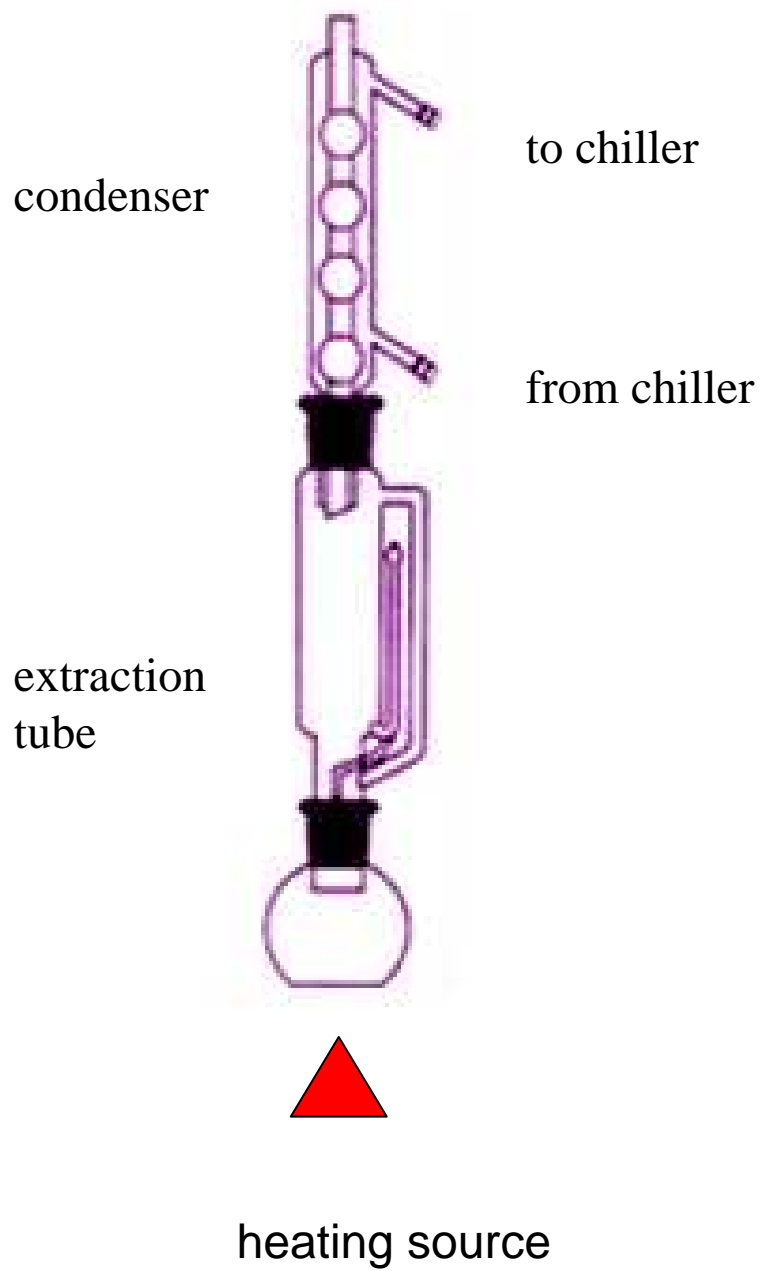
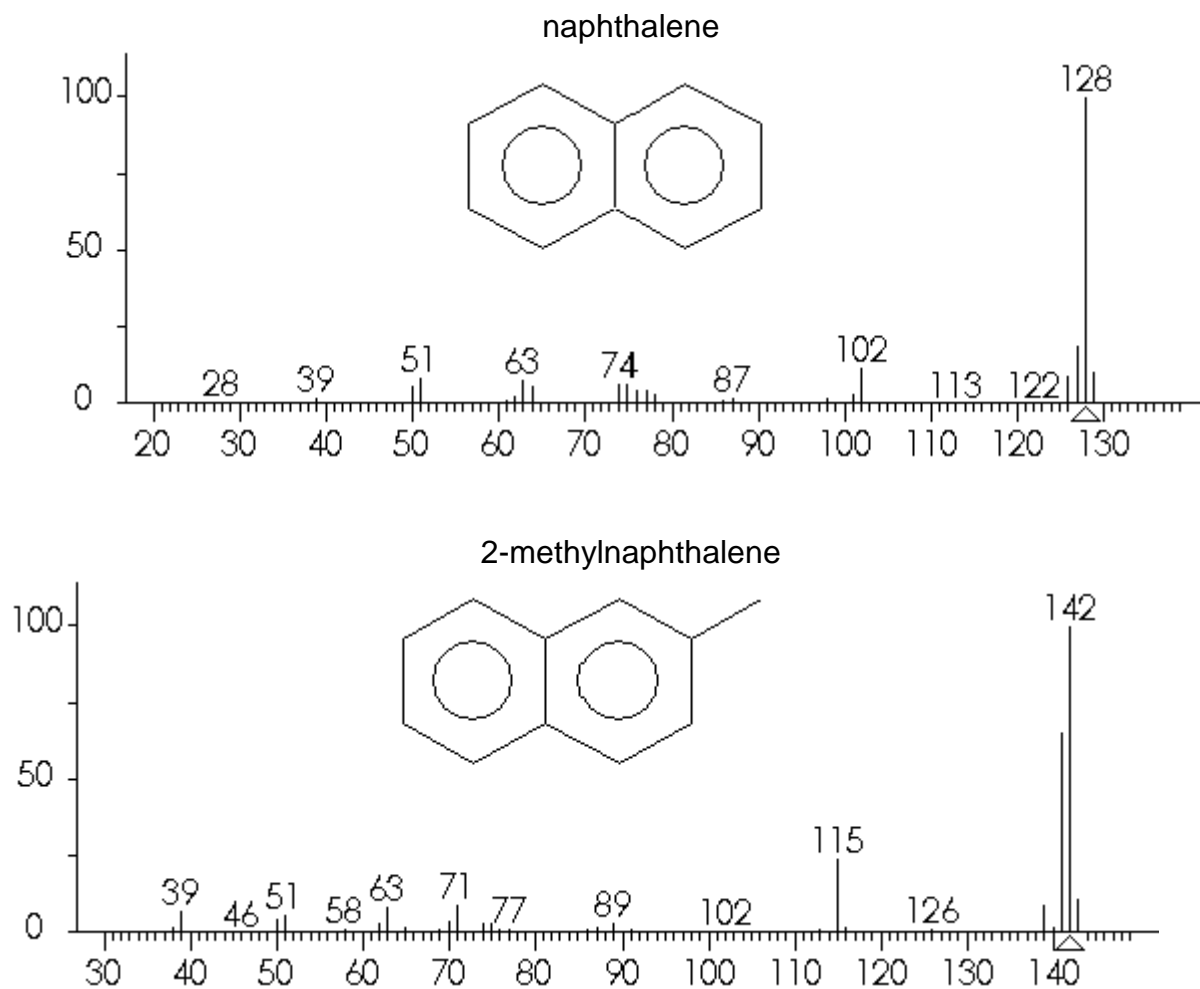
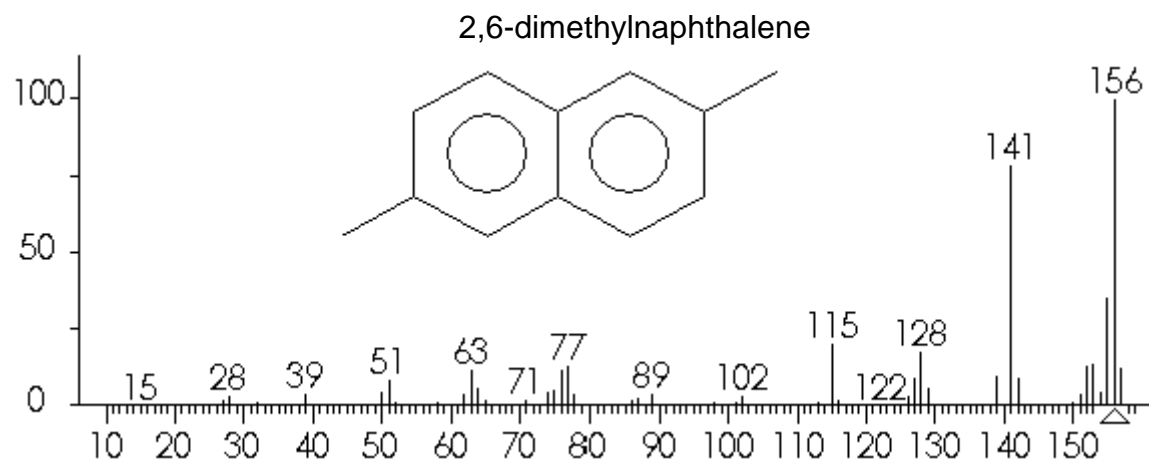
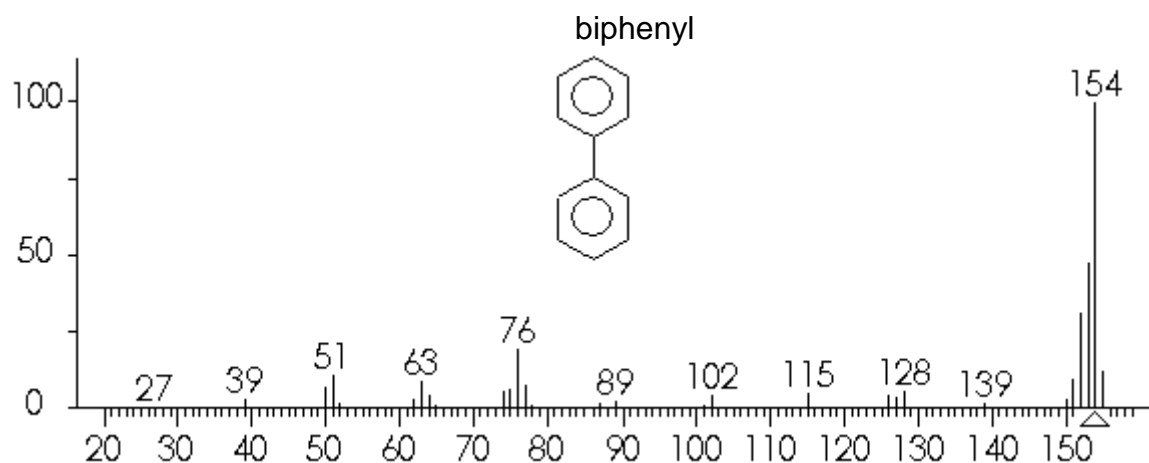
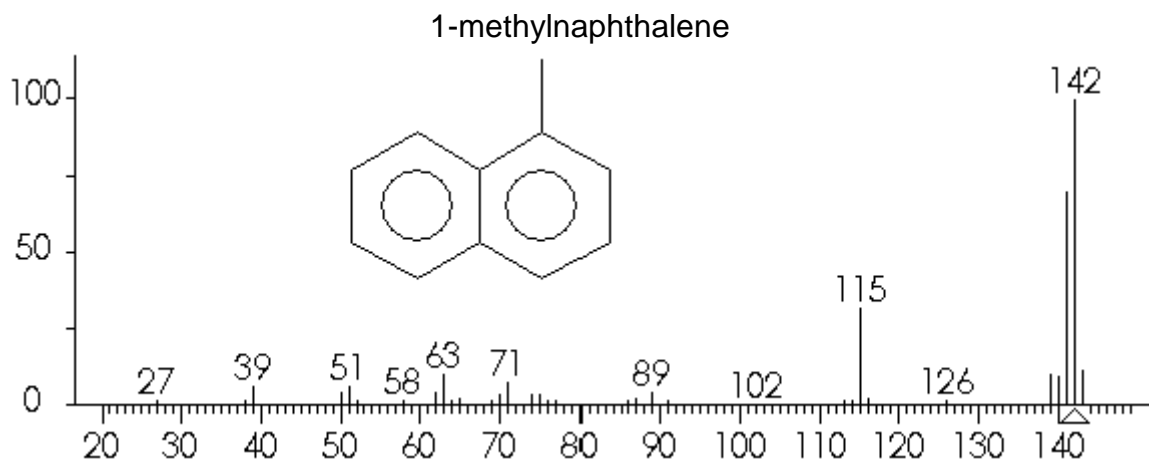
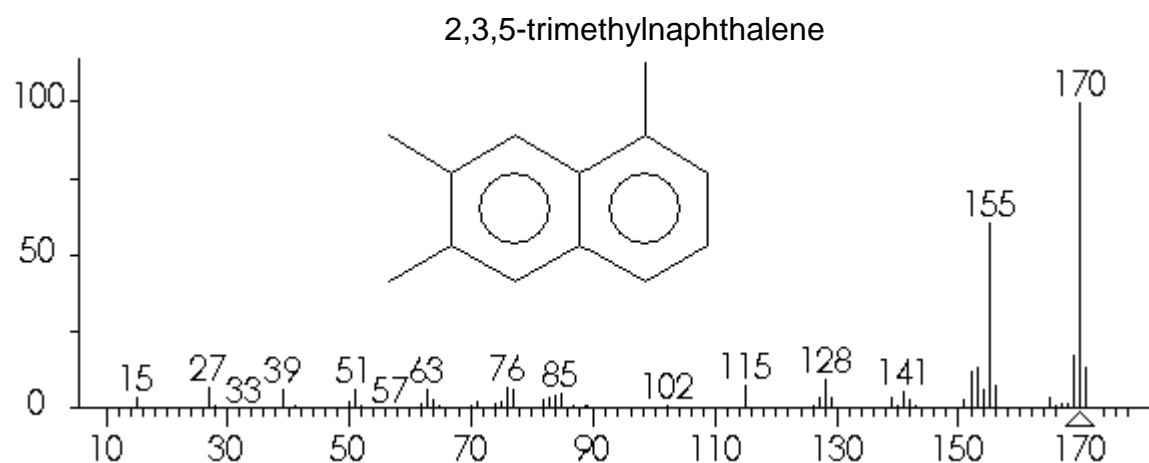
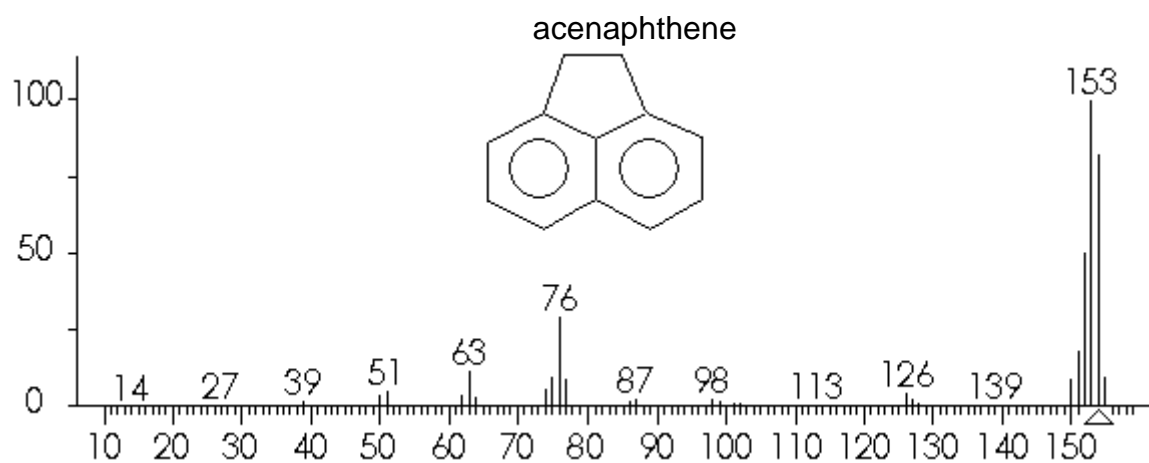
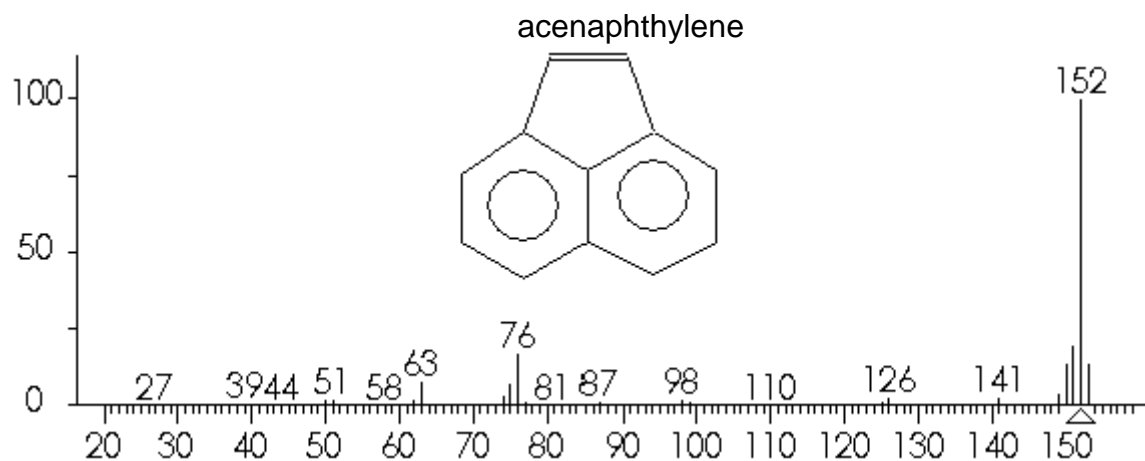


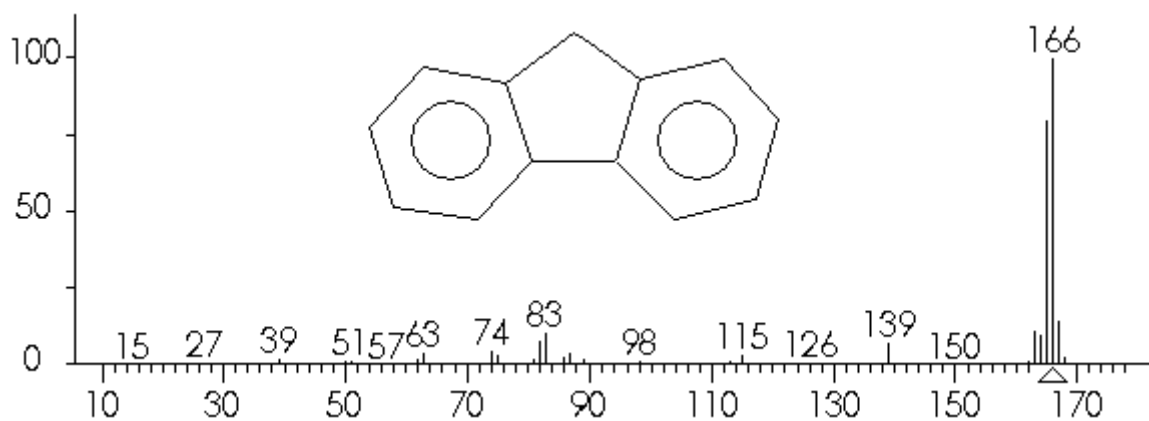
Figure 3 The molecular structure and the mass spectrum of the PAH compounds analyzed by GC/MS in this method.



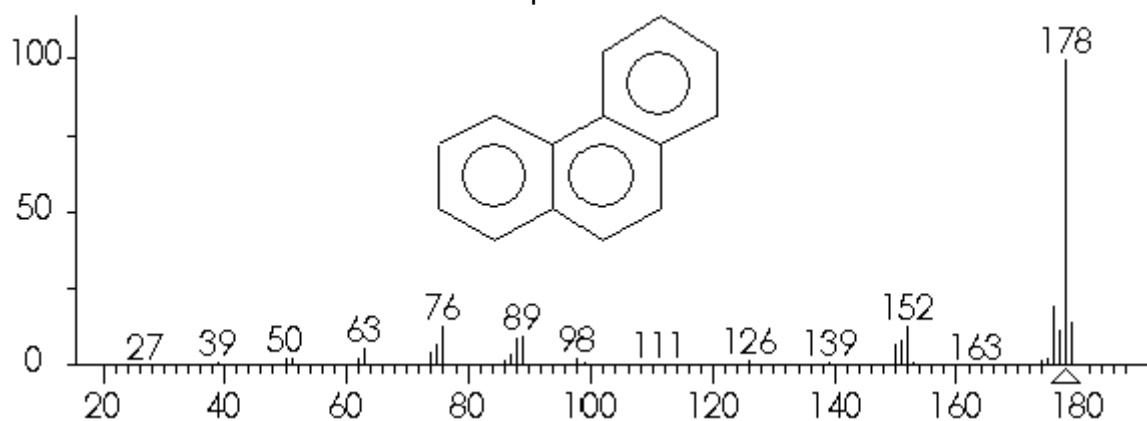




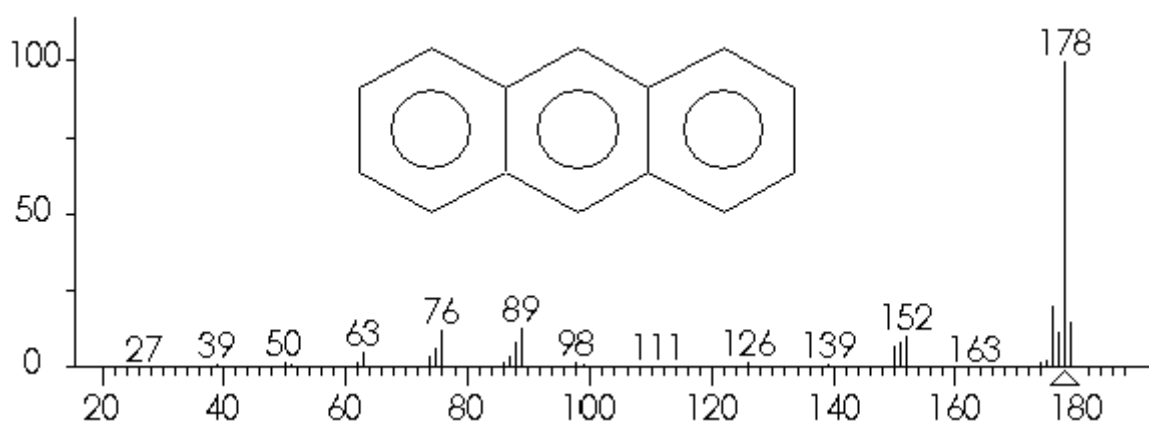
fluorene

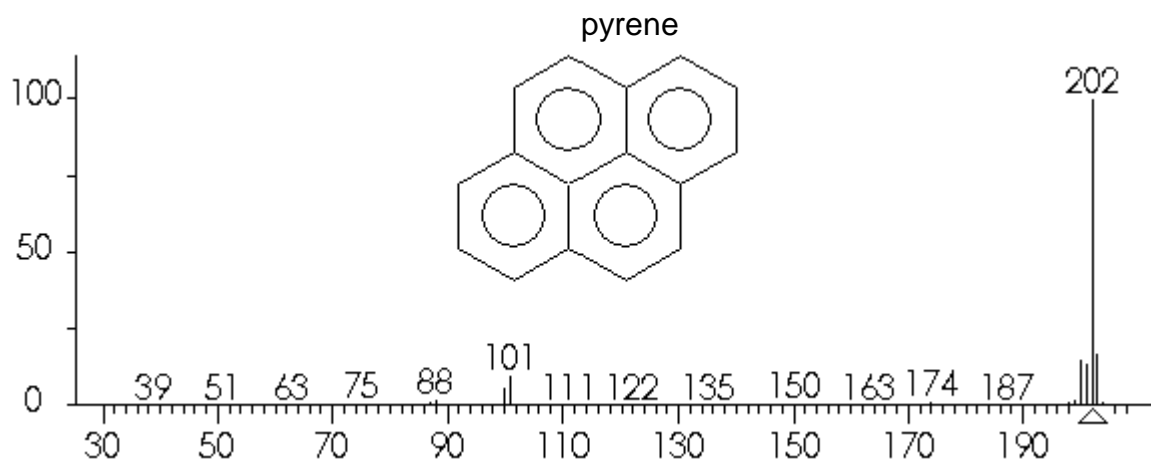
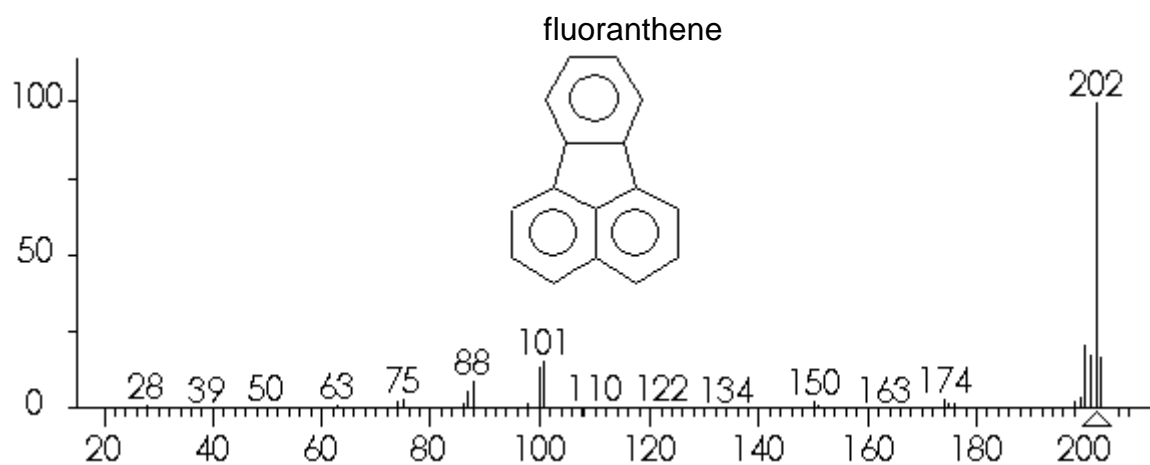
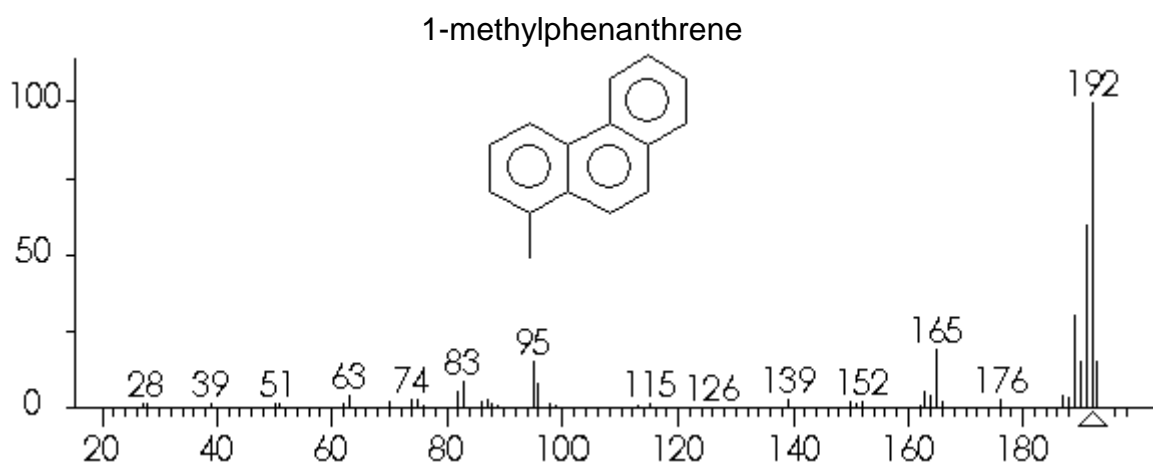


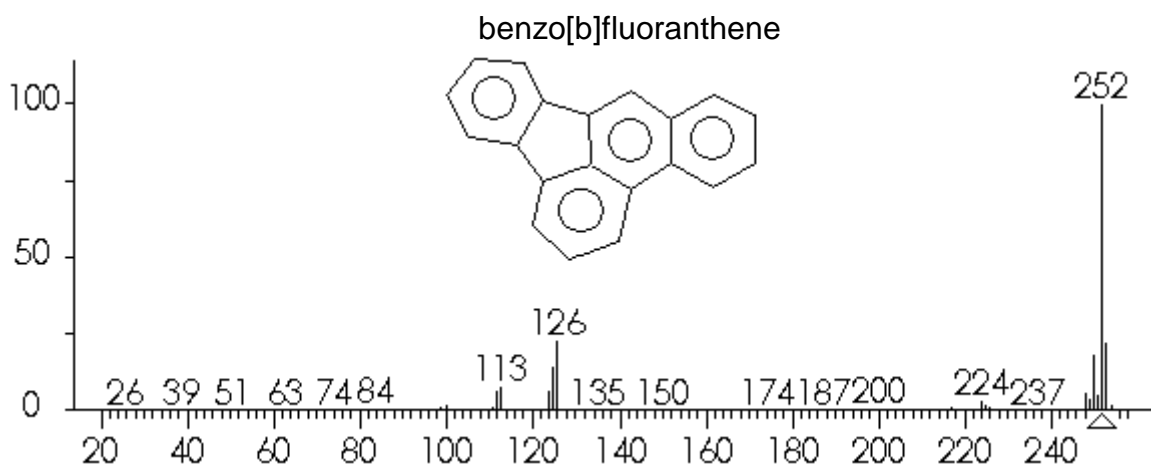
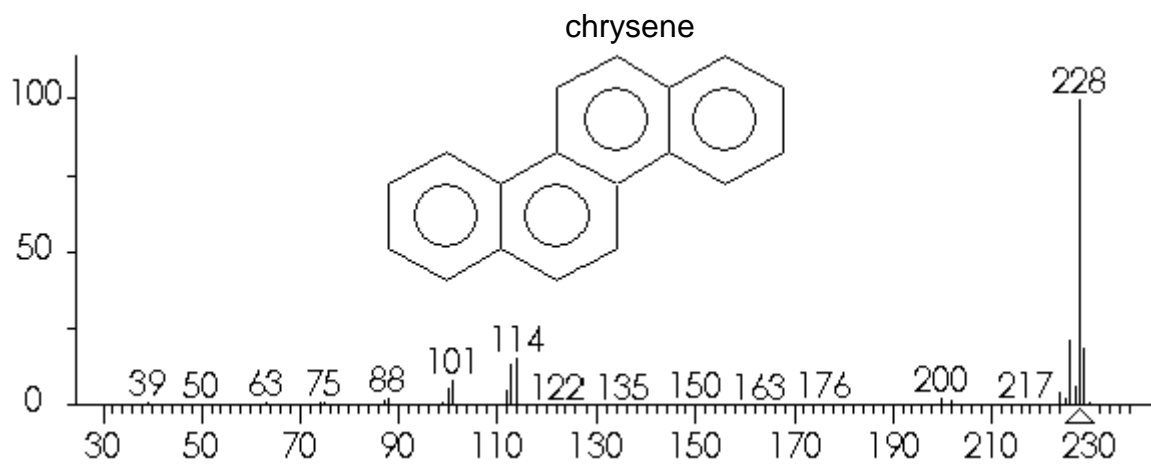
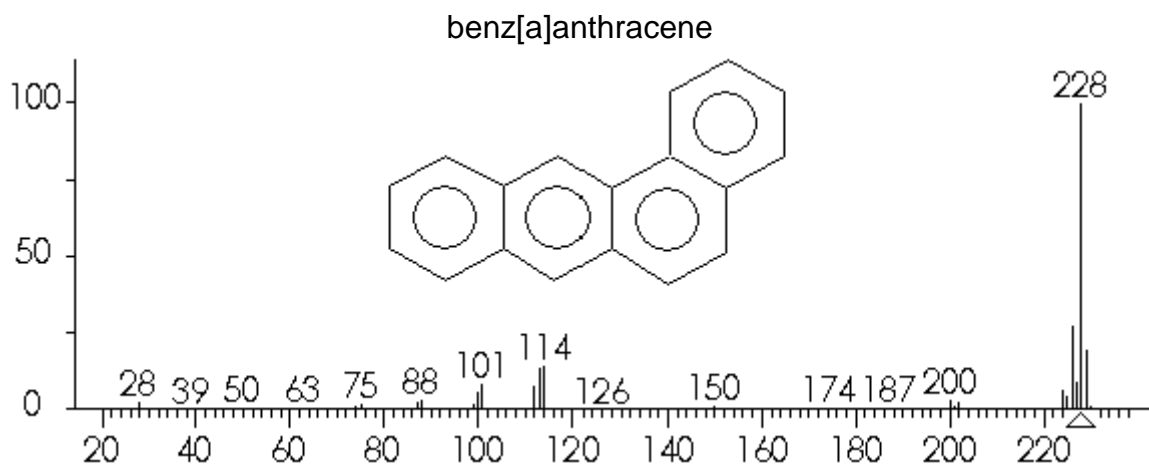
phenanthrene

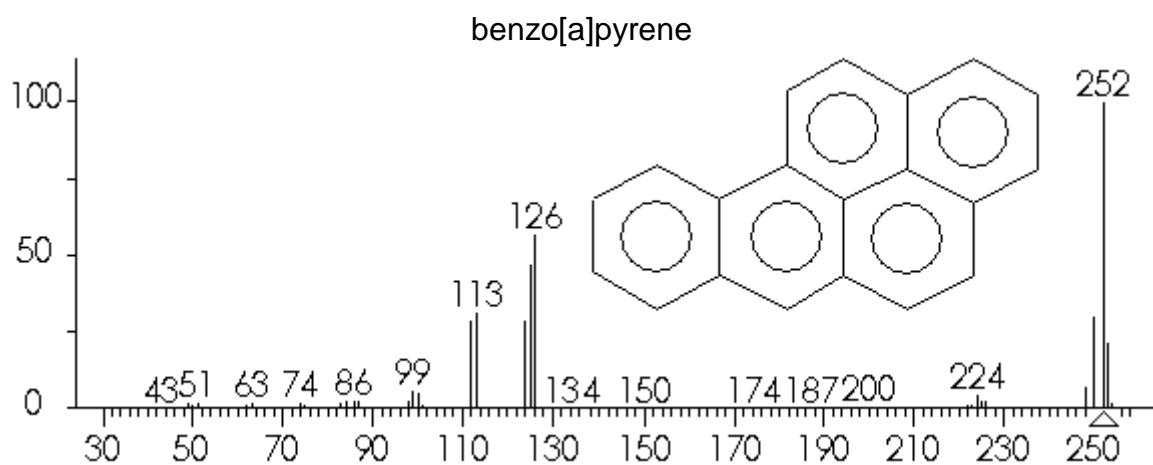
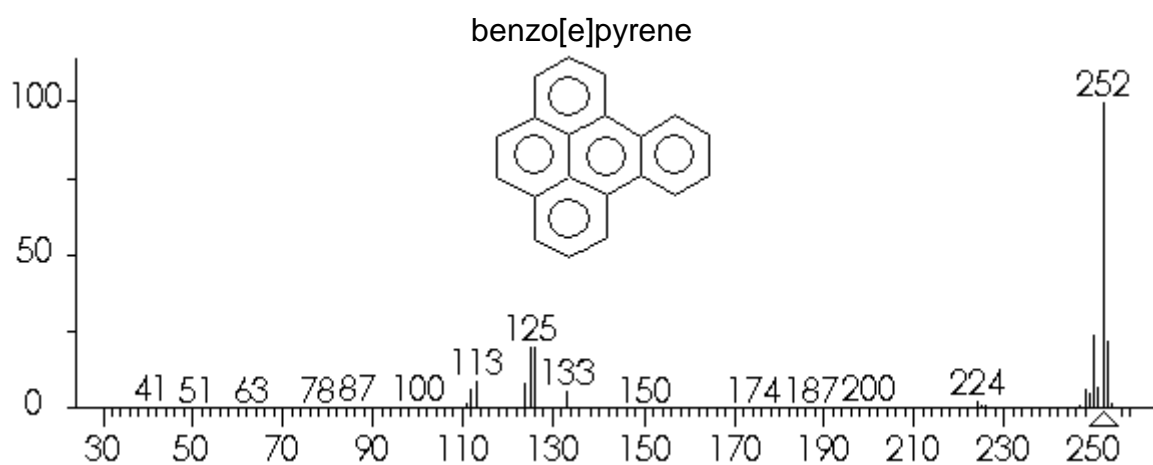
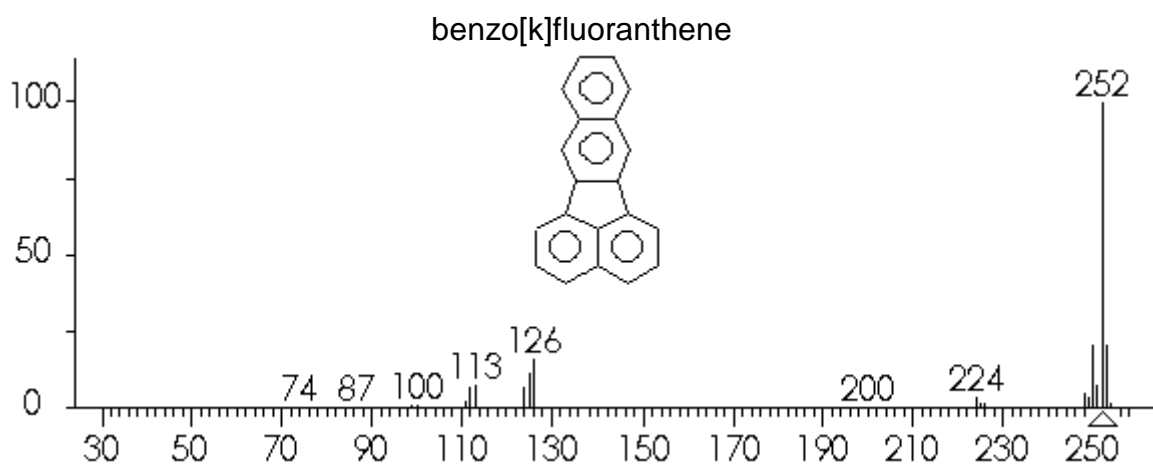


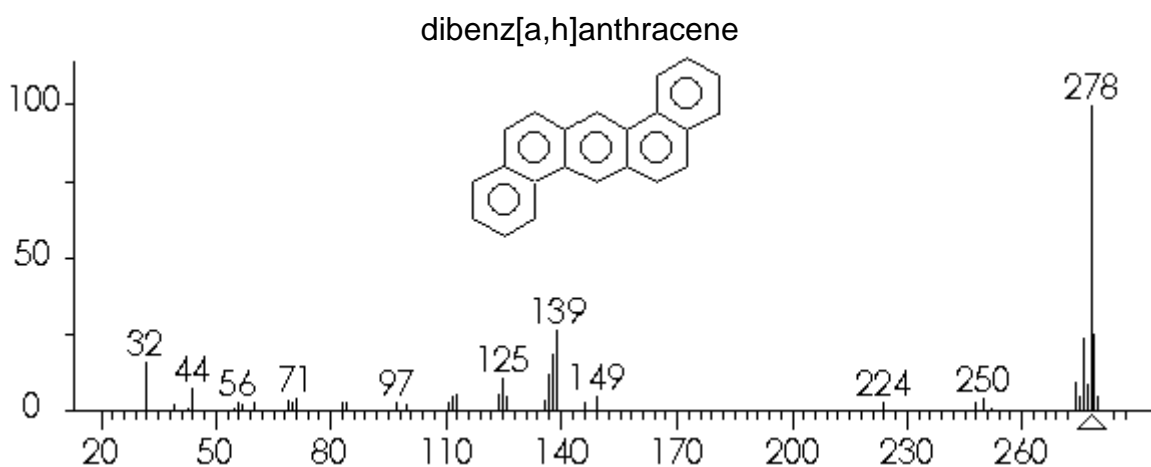
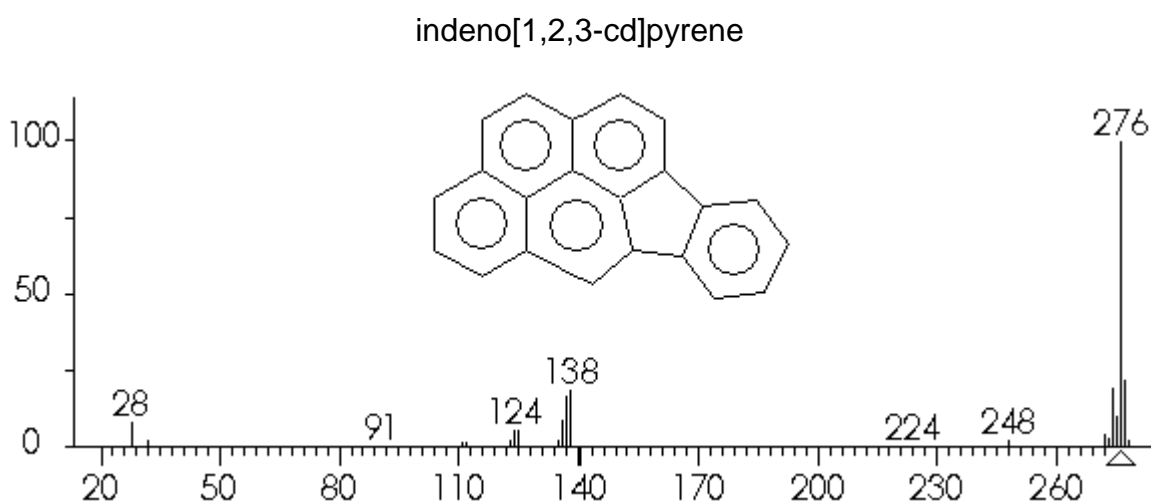
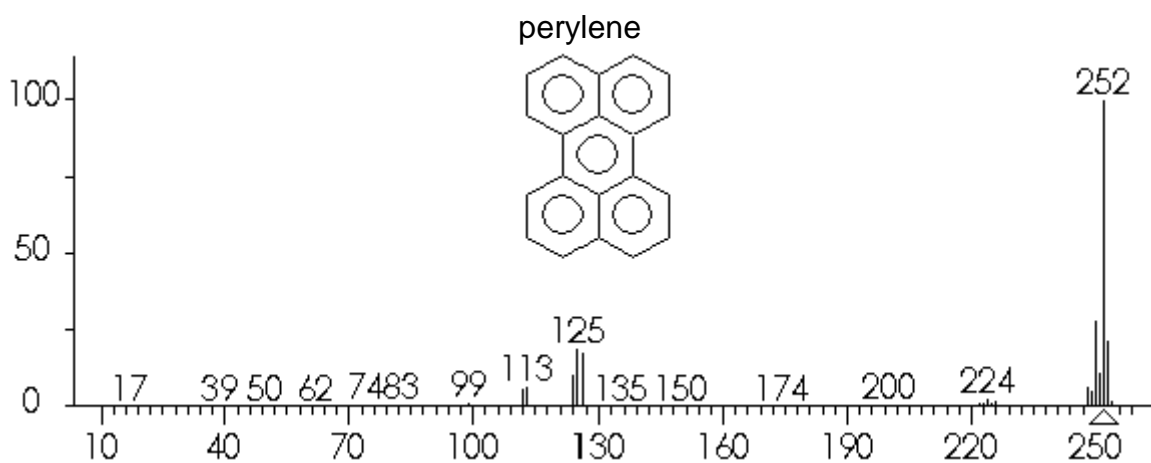
anthracene

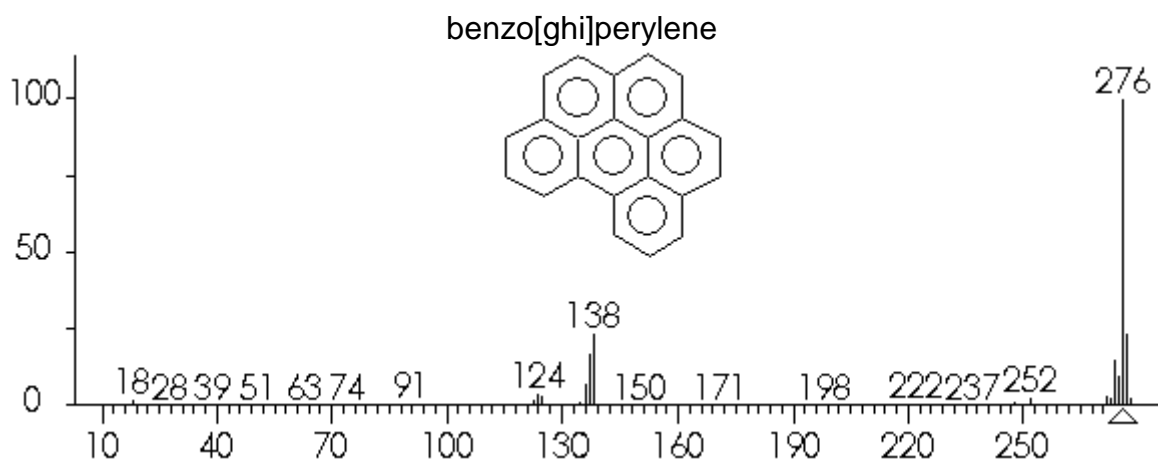












**Figure 4. The Total Ion Chromatogram (TIC) of
a Calibration Standard**

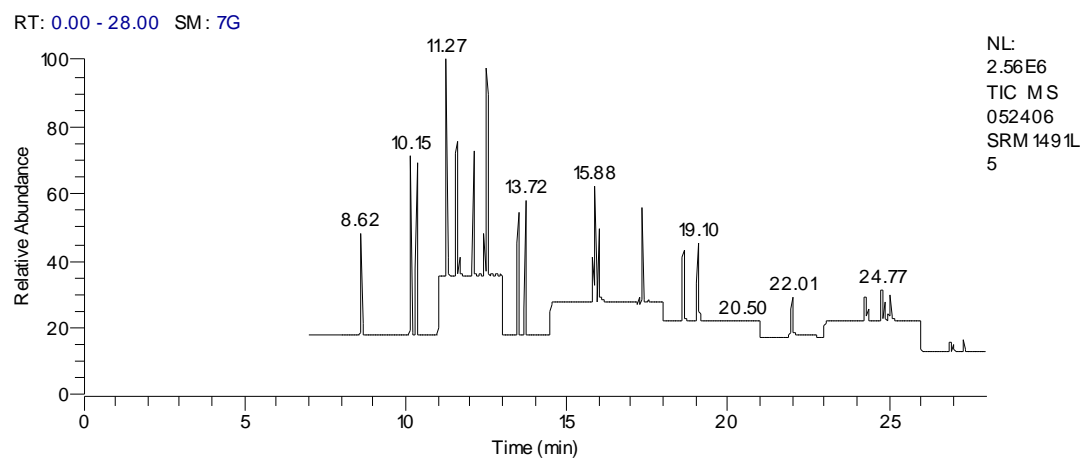


Figure 5. An example of the calibration curve for GC/MS analysis

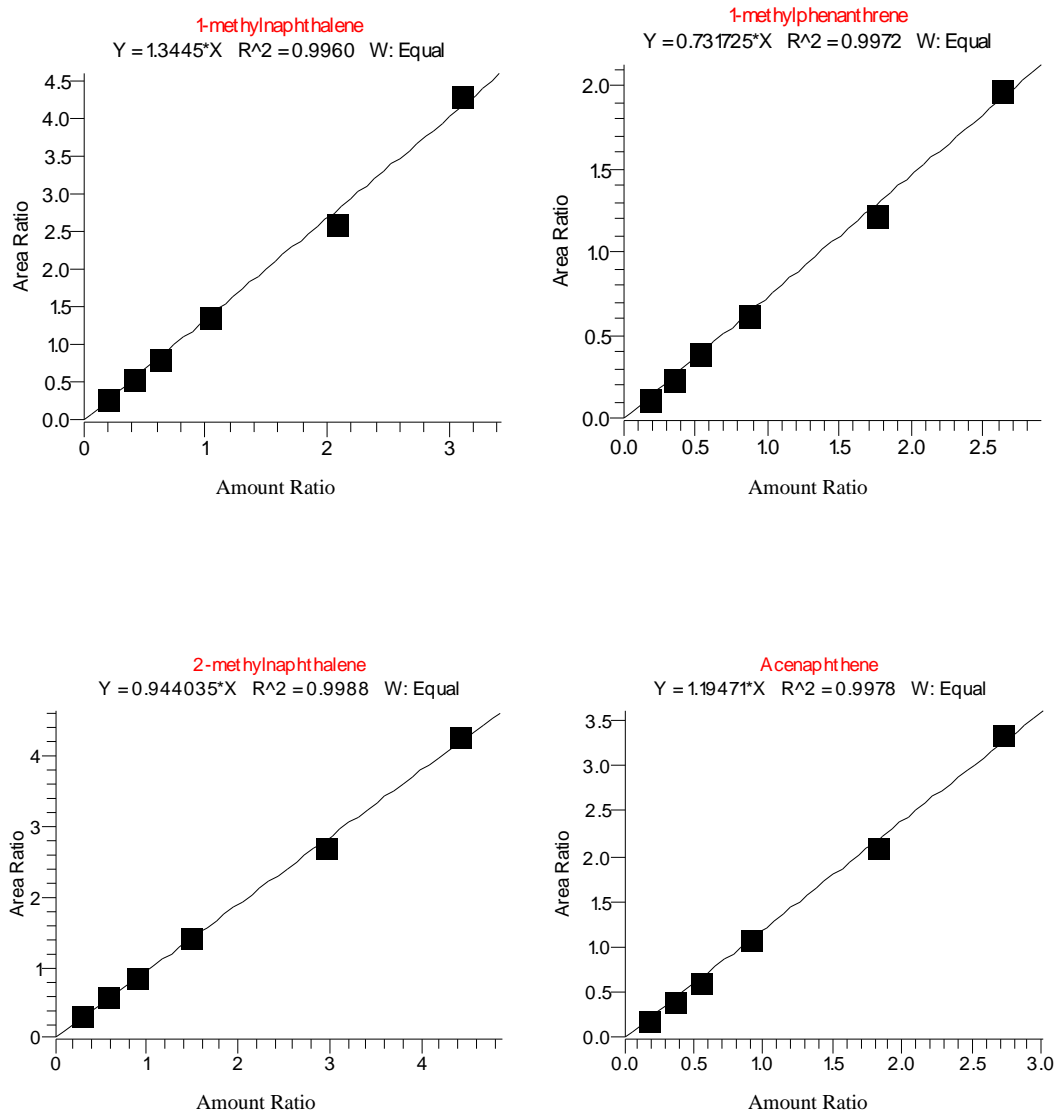


Figure 6. Sample report of the PAH analysis using GC/MS

PAH CONTENTS IN PM SAMPLE

Southern Laboratory Branch
Monitoring and Laboratory Division
Air Resources Board

Sample ID: TO2208B
Data File: 052406 TO2208B
Curr Data Path: C:\Xcalibur\Data\shh2006\05_2006\\
Operator: PM
Acquisition Date: 05/25/06 05:13:43
Inst Method: C:\Xcalibur\methods\SIM_SRM1491.meth
Extract Vol (mL): 1.00

Target Analyte	Calculated Amount (ng/mL)	Remarks
Naphthalene	0.136	
2-methylnaphthalene	0.198	
1-methylnaphthalene	0.078	
Biphenyl	N/A	
2,6-dimethyle-naphthalene	N/A	
Acenaphthylene	N/A	
Acenaphthene-d10	N/A	
Acenaphthene	N/A	
2,3,5-trimethyl-naphthalene	0.062	
Fluorene	0.055	
Phenathrene-d10	N/A	
Phenanthrene	2.116	
Anthracene	N/A	
1-methylephenanthrene	3.913	
Fluoranthene	1.282	
Pyrene-d10	N/A	
Pyrene	0.000	
Benz[a]anthracene	N/A	
Chrysene-d12	N/A	
Chrysene	N/A	
Benzo[b]fluoranthene	N/A	
Benzo[k]fluoranthene	N/A	
Benzo[e]pyrene	0.000	
Benzo[a]pyrene	N/A	
Perylene-d12	N/A	
Perylene	N/A	
Indeno[1,2,3-cd]pyrene	N/A	
Dibenz[a,h]anthracene	N/A	
Benzo[ghi]perylene	N/A	

Table 1 Target PAHs and formulae

	Compound	Formula
1	Naphthalene	C ₁₀ H ₈
2	2-Methylnaphthalene	C ₁₁ H ₁₀
3	1-Methylnaphthalene	C ₁₁ H ₁₀
4	Biphenyl*	C ₁₂ H ₁₀
5	2,6-Dimethylnaphthalene	C ₁₂ H ₁₂
6	Acenaphthylene	C ₁₂ H ₈
7	Acenaphthene	C ₁₂ H ₁₀
8	2,3,5-Trimethylnaphthalene	C ₁₃ H ₁₄
9	Fluorene	C ₁₃ H ₁₀
10	Phenanthrene	C ₁₄ H ₁₀
11	Anthracene	C ₁₄ H ₁₀
12	1-Methylphenanthrene	C ₁₅ H ₁₂
13	Fluoranthene	C ₁₆ H ₁₀
14	Pyrene	C ₁₆ H ₁₀
15	Benz[a]anthracene	C ₁₈ H ₁₂
16	Chrysene	C ₁₈ H ₁₂
17	Benzo[b]fluoranthene	C ₂₀ H ₁₂
18	Benzo[k]fluoranthene	C ₂₀ H ₁₂
19	Benzo[e]pyrene	C ₂₀ H ₁₂
20	Benzo[a]pyrene	C ₂₀ H ₁₂
21	Perylene	C ₂₀ H ₁₂
22	Indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂
23	Debenz[a,h]anthracene	C ₂₂ H ₁₄
24	Benzo[ghi]perylene	C ₂₂ H ₁₂

* biphenyl is not a PAH

Table 2 Target PAHs and their Recovery Standard

Compound	Recovery standard
Naphthalene	Naphthalene - d8
2-Methylnaphthalene	2-Methylnaphthalene-d10
1-Methylnaphthalene	2-Methylnaphthalene-d10
Biphenyl*	Acenaphthylene-d8
2,6-Dimethylnaphthalene	2,6-Dimethylnaphthalene-d12
Acenaphthylene	Acenaphthylene-d8
Acenaphthene	Acenaphthylene-d8
2,3,5-Trimethylnaphthalene	Acenaphthylene-d8
Fluorene	Acenaphthylene-d8
Phenanthrene	Anthracene- d10
Anthracene	Anthracene- d10
1-Methylphenanthrene	Anthracene- d10
Fluoranthene	Fluoranthene-d10
Pyrene	Fluoranthene-d10
Benz[a]anthracene	Benz[a]anthracene-d12
Chrysene	Benz[a]anthracene-d12
Benzo[b]fluoranthene	Benzo[b]fluoranthene-d12
Benzo[k]fluoranthene	Benzo[k]fluoranthene-d12
Benzo[e]pyrene	Benzo[a]pyrene-d12
Benzo[a]pyrene	Benzo[a]pyrene-d12
Perylene	Benzo[a]pyrene-d12
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene-d12
Debenz[a,h]anthracene	Debenz[a,h]anthracene-d14
Benzo[ghi]perylene	Benzo[ghi]perylene-d12

Table 3 PAH Calibration standards

Unit: ng/mL

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7
Naphthalene	0.052	0.17	0.34	0.52	0.86	1.72	2.58
2-Methylnaphthalene	0.089	0.30	0.59	0.89	1.48	2.95	4.43
1-Methylnaphthalene	0.062	0.21	0.42	0.62	1.04	2.08	3.11
Biphenyl*	0.053	0.18	0.35	0.53	0.88	1.75	2.63
2,6-Dimethylnaphthalene	0.054	0.18	0.36	0.54	0.90	1.80	2.70
Acenaphthylene	0.052	0.17	0.35	0.52	0.87	1.74	2.61
Acenaphthene	0.055	0.18	0.36	0.55	0.91	1.82	2.73
2,3,5-Trimethylnaphthalene	0.050	0.17	0.33	0.50	0.83	1.65	2.48
Fluorene	0.055	0.18	0.36	0.55	0.91	1.82	2.73
Phenanthrene	0.053	0.18	0.35	0.53	0.88	1.75	2.63
Anthracene	0.059	0.20	0.39	0.59	0.98	1.96	2.93
1-Methylphenanthrene	0.053	0.18	0.35	0.53	0.88	1.75	2.63
Fluoranthene	0.044	0.15	0.30	0.44	0.74	1.48	2.22
Pyrene	0.044	0.15	0.29	0.44	0.74	1.47	2.21
Benz[a]anthracene	0.027	0.09	0.18	0.27	0.45	0.90	1.35
Chrysene	0.053	0.18	0.35	0.53	0.88	1.76	2.64
Benzo[b]fluoranthene	0.039	0.13	0.26	0.39	0.66	1.31	1.97
Benzo[k]fluoranthene	0.042	0.14	0.28	0.42	0.70	1.39	2.09
Benzo[e]pyrene	0.042	0.14	0.28	0.42	0.70	1.41	2.11
Benzo[a]pyrene	0.051	0.17	0.34	0.51	0.85	1.70	2.55
Perylene	0.053	0.18	0.36	0.53	0.89	1.78	2.67
Indeno[1,2,3-cd]pyrene	0.047	0.16	0.31	0.47	0.79	1.57	2.36
Debenz[a,h]anthracene	0.039	0.13	0.26	0.39	0.65	1.30	1.94
Benzo[ghi]perylene	0.040	0.13	0.26	0.40	0.66	1.32	1.98

Table 4 Target PAHs and their Internal Standard (IS)

Compound	Internal standard
Naphthalene	Acenaphthene-d10
2-Methylnaphthalene	Acenaphthene-d10
1-Methylnaphthalene	Acenaphthene-d10
Biphenyl*	Acenaphthene-d10
2,6-Dimethylnaphthalene	Acenaphthene-d10
Acenaphthylene	Acenaphthene-d10
Acenaphthene	Acenaphthene-d10
2,3,5-Trimethylnaphthalene	Acenaphthene-d10
Fluorene	Acenaphthene-d10
Phenanthrene	Phenanthrene-d10
Anthracene	Phenanthrene-d10
1-Methylphenanthrene	Phenanthrene-d10
Fluoranthene	Pyrene-d10
Pyrene	Pyrene-d10
Benz[a]anthracene	Pyrene-d10
Chrysene	Chrysene-d12 or Perylene-d12
Benzo[b]fluoranthene	Chrysene-d12 or Perylene-d12
Benzo[k]fluoranthene	Chrysene-d12 or Perylene-d12
Benzo[e]pyrene	Chrysene-d12 or Perylene-d12
Benzo[a]pyrene	Chrysene-d12 or Perylene-d12
Perylene	Chrysene-d12 or Perylene-d12
Indeno[1,2,3-cd]pyrene	Chrysene-d12 or Perylene-d12
Debenz[a,h]anthracene	Chrysene-d12 or Perylene-d12
Benzo[ghi]perylene	Chrysene-d12 or Perylene-d12

Table 5 Target PAHs and their Characteristic Ions for Quantification

Compound	Primary Ion	Secondary ion(s)
Naphthalene	128	127
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141
Biphenyl*	154	153,152
2,6-Dimethylnaphthalene	156	155,154
Acenaphthylene	152	151
Acenaphthene	153	154,152
2,3,5-Trimethylnaphthalene	155	170,165
Fluorene	166	165
Phenanthrene	178	177,176
Anthracene	178	177,176
1-Methylphenanthrene	192	191
Fluoranthene	202	201,200
Pyrene	202	201
Benz[a]anthracene	228	229
Chrysene	228	229
Benzo[b]fluoranthene	252	250,253
Benzo[k]fluoranthene	252	250,253
Benzo[e]pyrene	252	250,253
Benzo[a]pyrene	252	250,253
Perylene	252	250,253
Indeno[1,2,3-cd]pyrene	276	277
Debenz[a,h]anthracene	278	276
Benzo[ghi]perylene	276	277

* Biphenyl is not a PAH compound

Table 6 Characteristic Ions for Internal and Recovery Standards

Compound	Type*	Primary Ion	Secondary ion(s)
Naphthalene-d8	RS	136	135
2-Methylnaphthalene-d10	RS	152	150
2,6-Dimethylnaphthalene-d12	RS	168	150
Acenaphthylene-d8	RS	160	159
Acenaphthene-d10	IS	164	163
Phenanthrene-d10	IS	188	189
Anthracene-d10	RS	188	189
Fluoranthene-d10	RS	212	211
Pyrene-d10	IS	212	211
Benz[a]anthracene-d12	RS	240	241
Chrysene-d12	IS	240	241
Benzo[b]fluoranthene-d12	RS	264	265
Benzo[k]fluoranthene-d12	RS	264	265
Benzo[a]pyrene-d12	RS	264	265
Perylene-d12	IS	264	265
Indeno[1,2,3-cd]pyrene-d12	RS	288	289
Debenz[a,h]anthracene-d14	RS	292	288
Benzo[ghi]perylene-d12	RS	288	289

RS: Recovery Standard**IS: Internal Standard**

